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Enabling Electric Aviation with Ultra High Energy Lithium Metal Batteries

John Lawson-PI (ARC), Tom Miller (GRC), James Wu (GRC), Bill Bennett (GRC), Charles Bauschlicher (ARC), Brianne Scheidegger (GRC), Justin Haskins (ARC)

NASA Aeronautics Research Mission Directorate (ARMD)

FY12 Seedling Phase I Technical Seminar

July 9-11, 2013

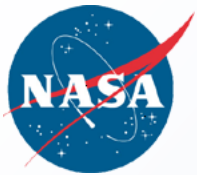


Electric Aviation

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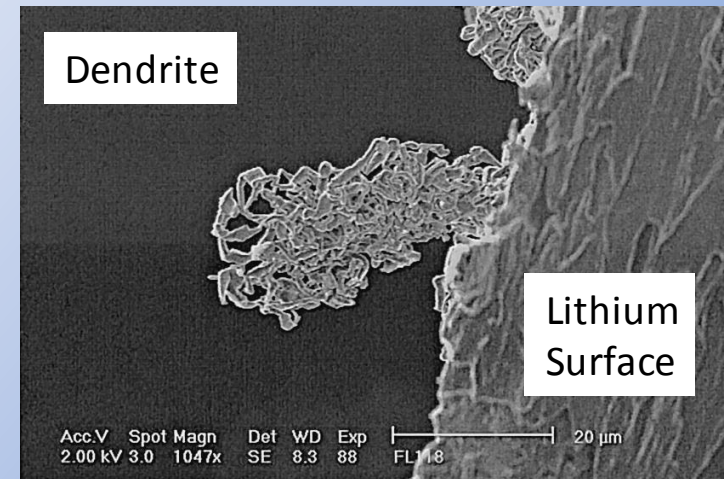
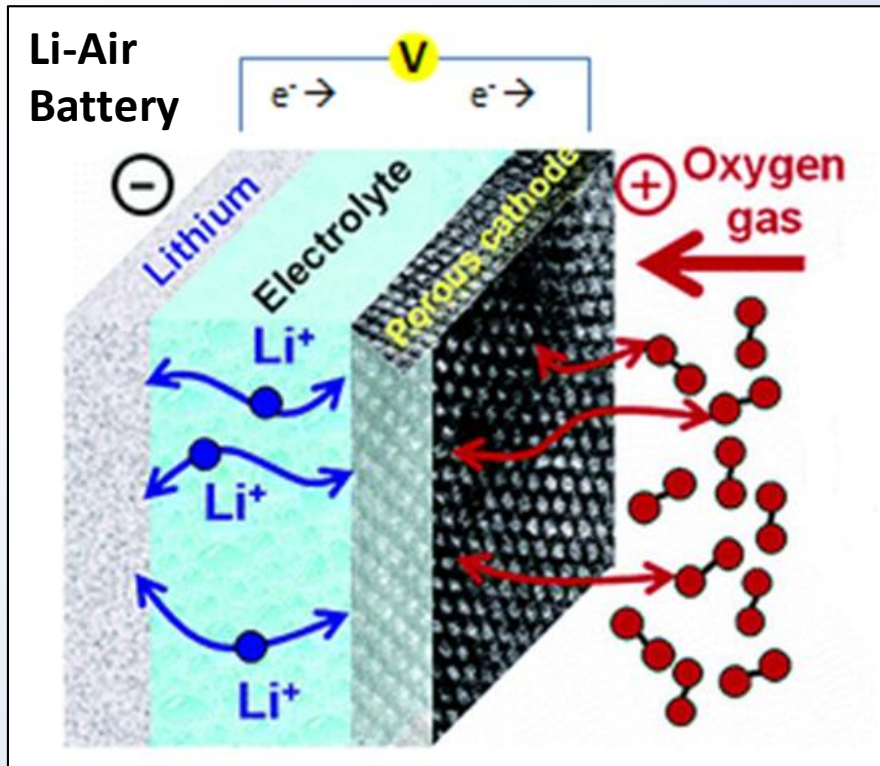
- **Green aviation:** high efficiency, low emissions, low noise
- **Solar Impulse:** largest technological limitation -- battery storage
- **Hybrid aircraft:** battery weight is significant limitation
- **Commercial aircraft:** battery powered onboard systems
- **Boeing 787 Dreamliner:** current battery electrolytes are flammable
- **Progress in electric aviation will depend on advances in ultra high energy, safe batteries**





Lithium Metal Anodes

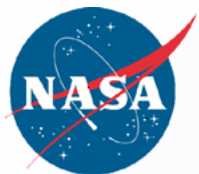
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Battery failure due to dendrites

F. Orsini et al., J. Power Sources 76, 19-29 (1998)

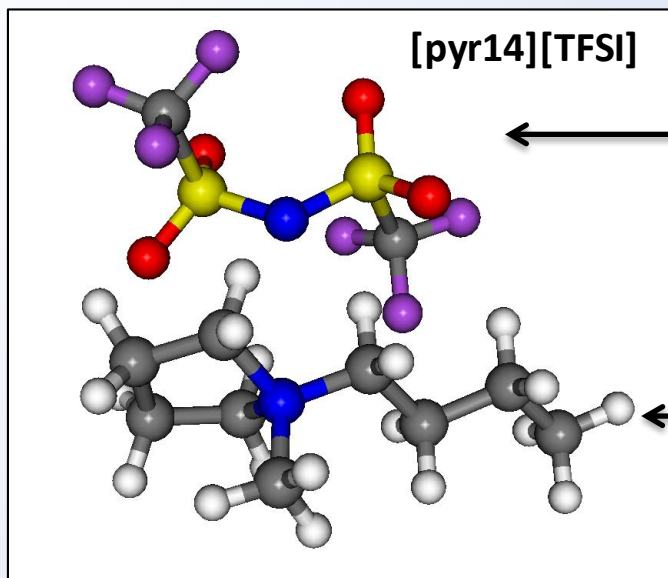
- Potential for **5X** increase in storage capacity
- **Safety** and **cycling** problems: issues for **Li-Air**, **Li-S**, etc
- **Holy Grail** of advanced battery technology



Ionic Liquid Electrolytes

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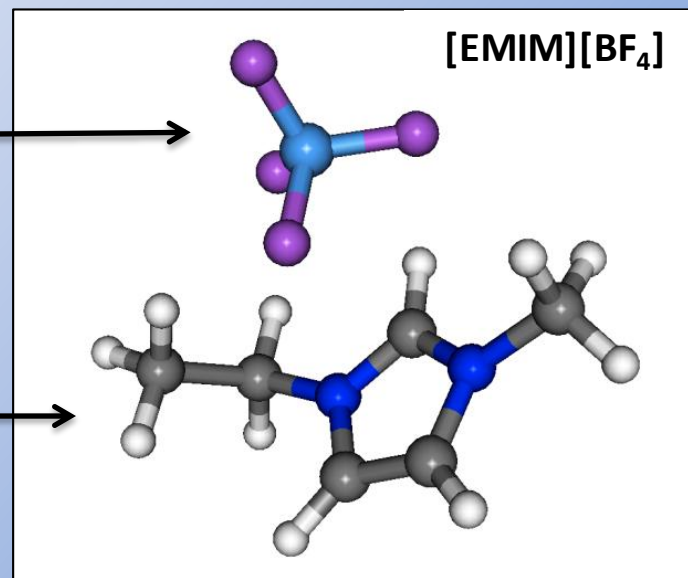
Good Cycling



Anions

Cations

Poor Cycling



Two Ionic Liquids are similar but have very different cycling behavior - **why?**

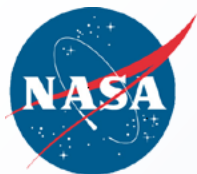
Fundamental understanding will enable design of ultra high energy batteries



Seedling Phase I Project

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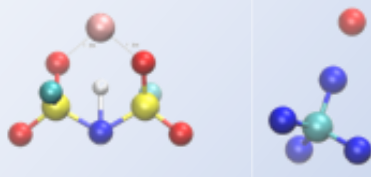
- **Innovation:** *computational predictive tool tightly coupled to experiments to accelerate fundamental understanding, screening and design of novel electrolytes for advanced batteries*
- **Application:** investigate two Ionic Liquid electrolytes (one good cycling and one poor) for Lithium metal anode batteries
- **Cross-Center, Multi-Disciplinary Team**
- **ARC Computational Materials Group:** modern computational material science methods
- **GRC Electrochemistry Branch:** wide-ranging experience in battery development experimental characterization
- **Benefit/Impact:** predictive tool for accelerated development of ultra high energy, safe batteries
- **Aggressive Work Plan** (12 milestones) -- all met or exceeded



Technical Approach

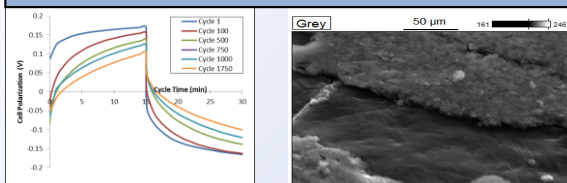
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I. Isolated Ionic Liquids



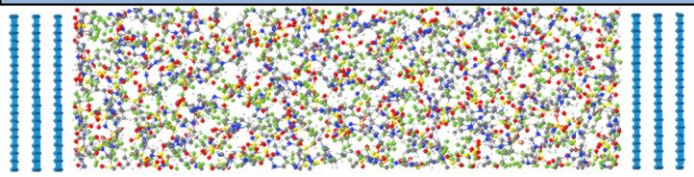
- Transport simulations
- Experimental validation

II. Experimental Cell Characterization



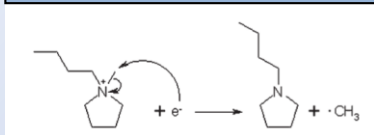
- Build cells
- Electrochemical characterization
- Surface layer identification

III. Ionic Liquid-Electrode interface



- Interface simulations with voltage
- Electric double layer structure

IV. Interfacial chemistry



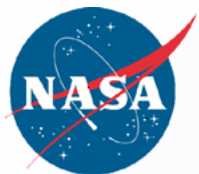
- Electrolyte surface decomposition
- Chemical pathways
- Surface layer formation



Phase I Seedling

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- I. **Isolated Ionic Liquids**
- II. Experimental Cell Characterization
- III. Ionic Liquid-Electrode Interfaces
- IV. Interfacial Chemistry
- V. Summary/Future Directions



Molecular Dynamics Simulations

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- Newton's law $F=ma$ for atoms

$$F = -\nabla E$$

- Bonded interactions:

$$E^{bond} + E^{angle} + E^{torsion}$$

- Non-bonded interactions:

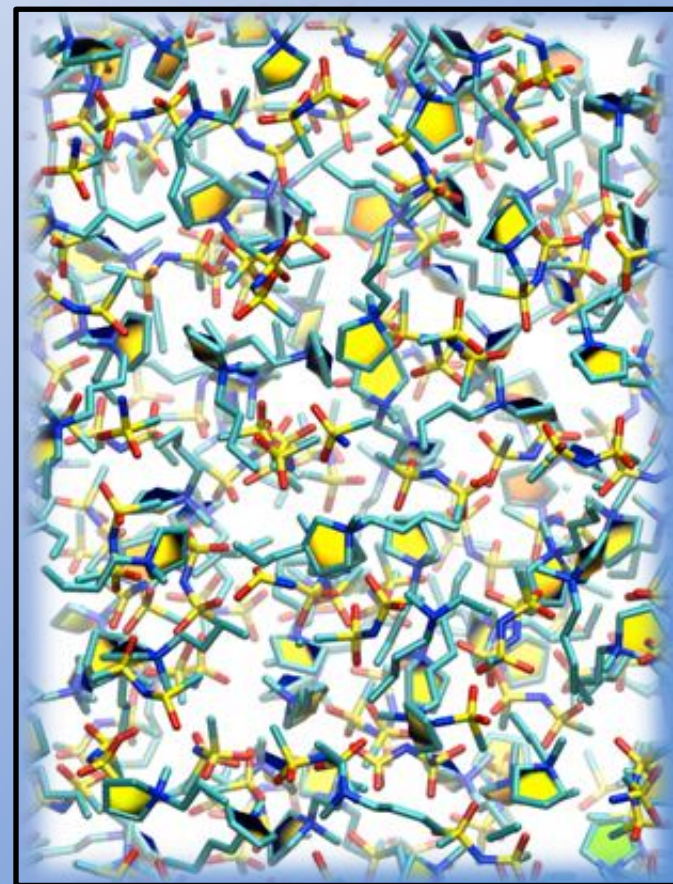
$$E^{vdw} + E^{qq}$$

- “Polarizable” interactions

$$E^{\mu q} + E^{\mu \mu}$$

- ***New polarizable software module for Ionic Liquid simulations developed***
- Massive datasets for analysis

[pyr14][TFSI]





Thermodynamics

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Well-established theoretical foundation (statistical mechanics)

Heat Capacity

$$C_P = \frac{\left. \frac{\partial (H + PV)}{\partial T} \right|_P}{k_B T^2} = \frac{\langle d(H + PV)^2 \rangle_{NPT}}{k_B T^2}$$

Isothermal Compressibility

$$b_T = \frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T = \frac{\langle dV^2 \rangle_{NPT}}{\langle V \rangle k_B T}$$

Thermal Expansion Coefficient

$$a_P = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = \frac{\langle dV d(H + PV) \rangle_{NPT}}{\langle V \rangle k_B T^2}$$

Thermal Pressure Coefficient

$$g_V = \left. \frac{\partial P}{\partial T} \right|_V = \frac{a_P}{b_T}$$



Transport Properties

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Non-equilibrium transport coefficients (fluctuation-dissipation theorems)

Diffusion

$$D \propto \lim_{t \rightarrow \infty} \frac{1}{t} \langle v(t)v(0) \rangle$$

Viscosity

$$\eta_{xy} \propto \lim_{t \rightarrow \infty} \frac{1}{t} \langle p_{xy}(t)p_{xy}(0) \rangle$$

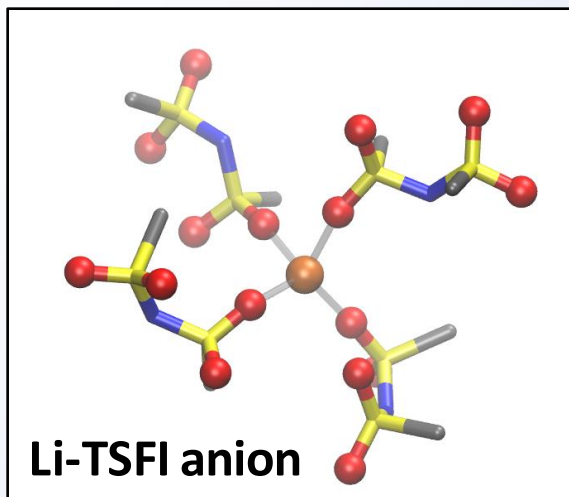
Ionic Conductivity

$$g_{IC} \propto \frac{d}{dt} \langle (qr(t) - qr(0))^2 \rangle$$

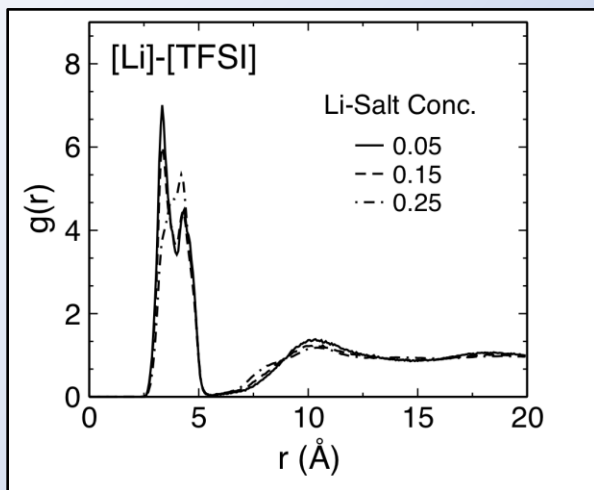
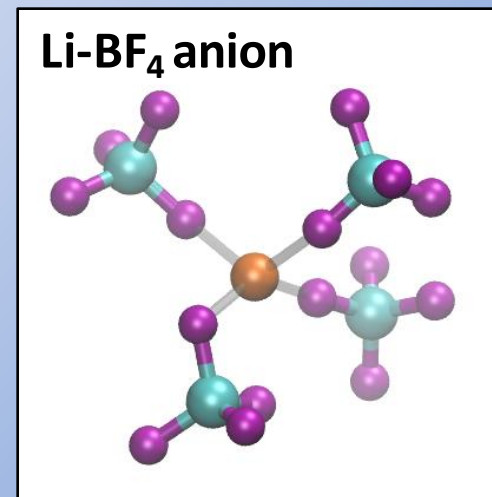


Example: Li^+ Ion Solvation Shell

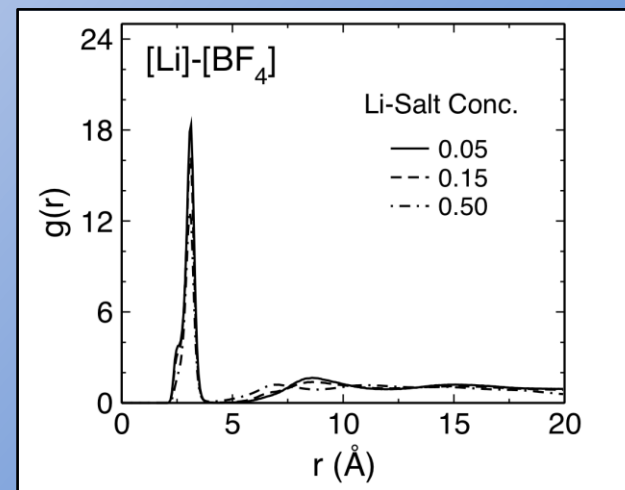
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Detailed
molecular
structure



Anion
distribution
about
Li ions

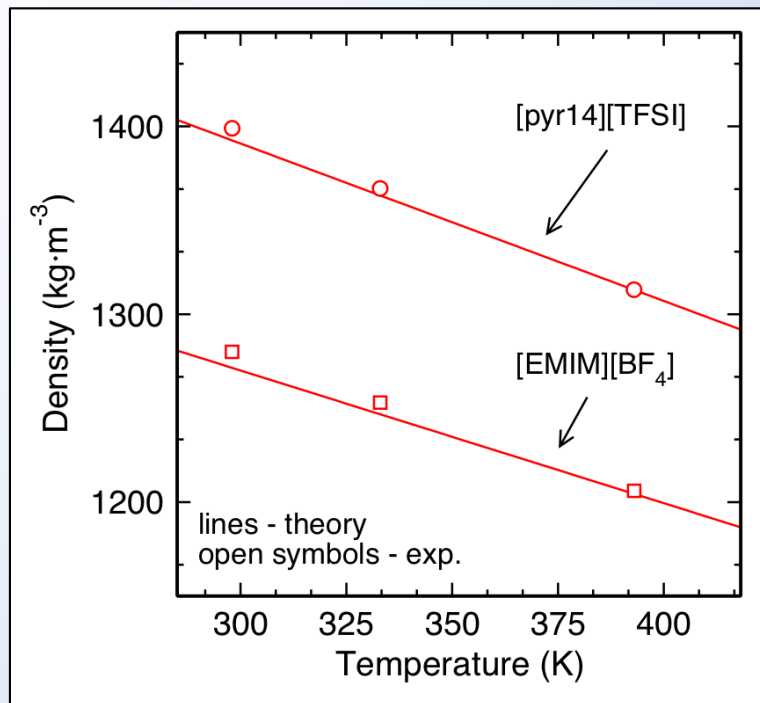




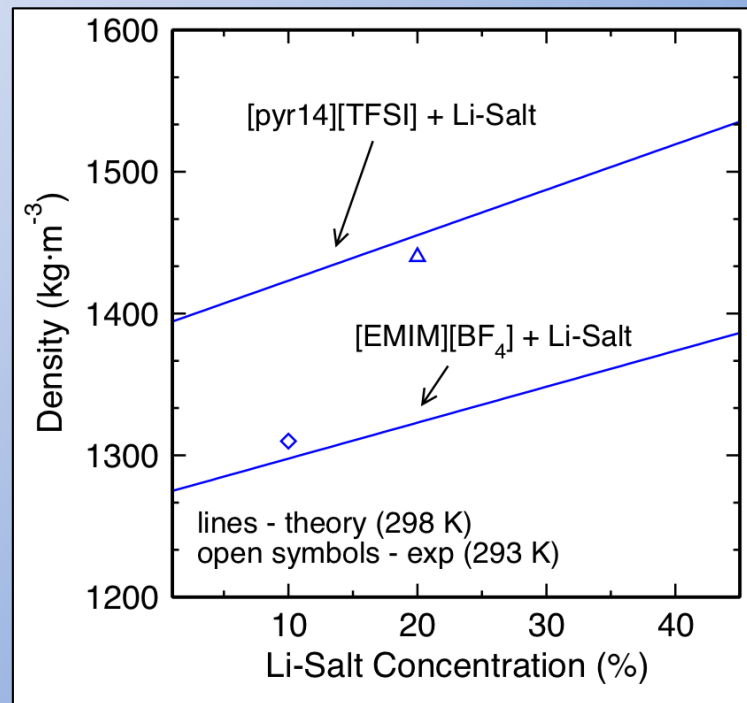
Density

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Neat Ionic Liquids



Lithiated Ionic Liquids



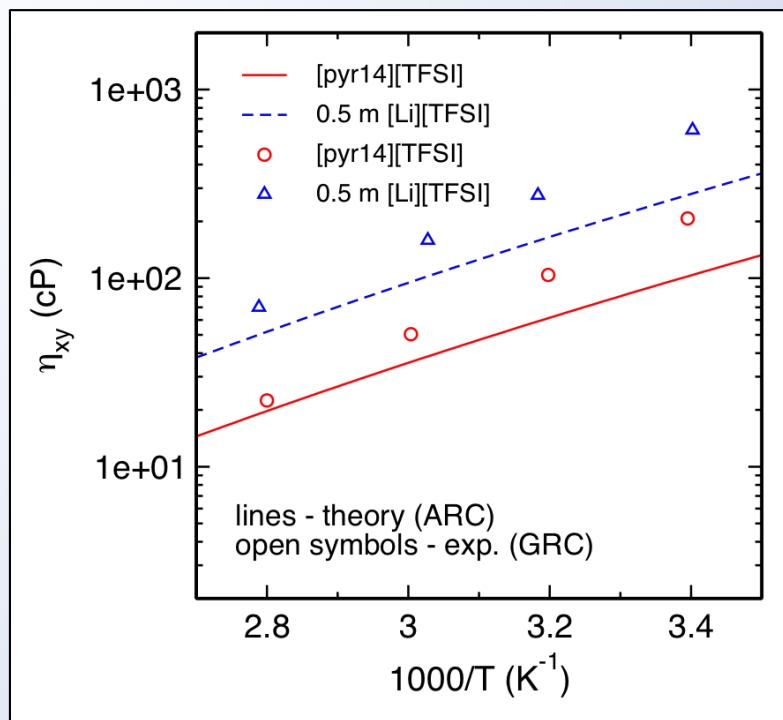
Excellent agreement with GRC experiments



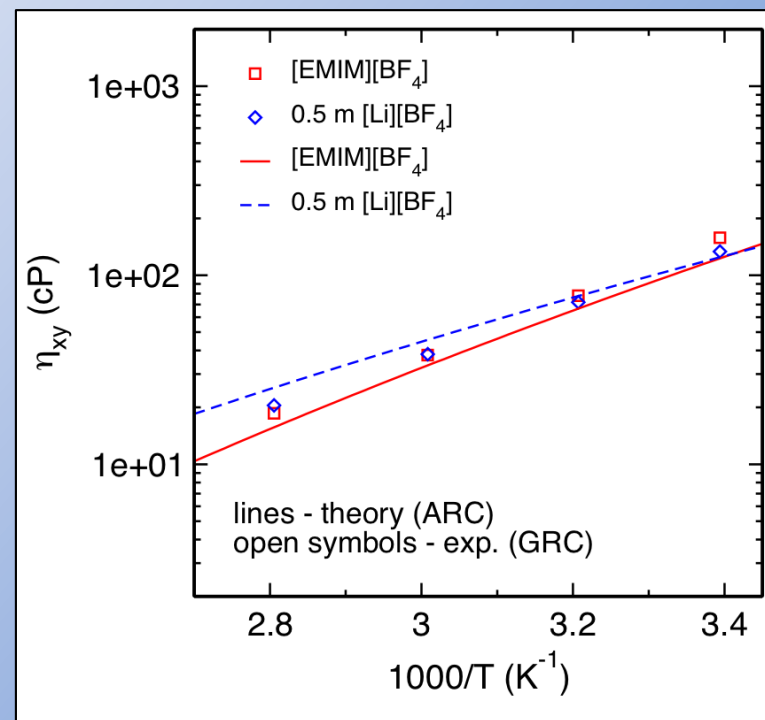
Viscosity

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[pyr14][TFSI]



[EMIM][BF₄]



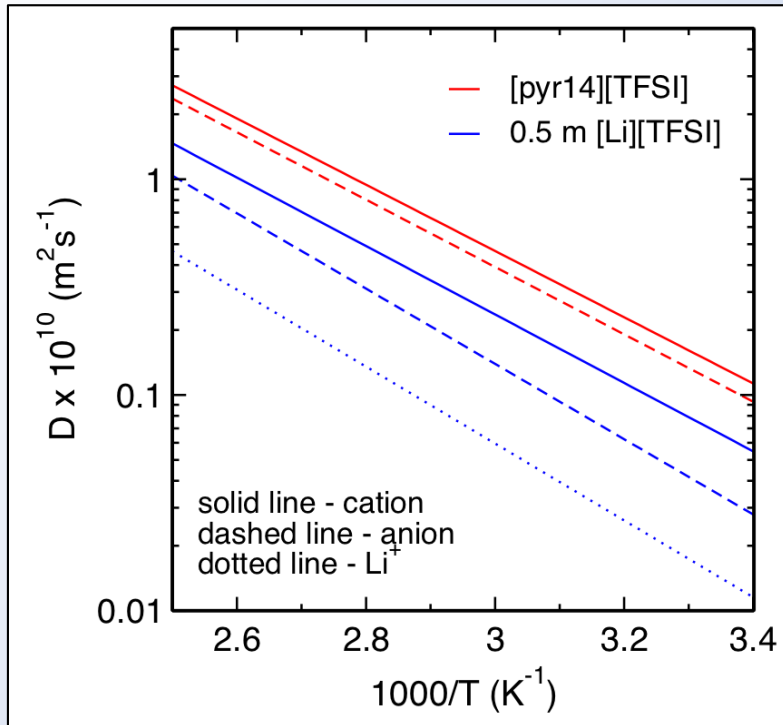
Good agreement with GRC results



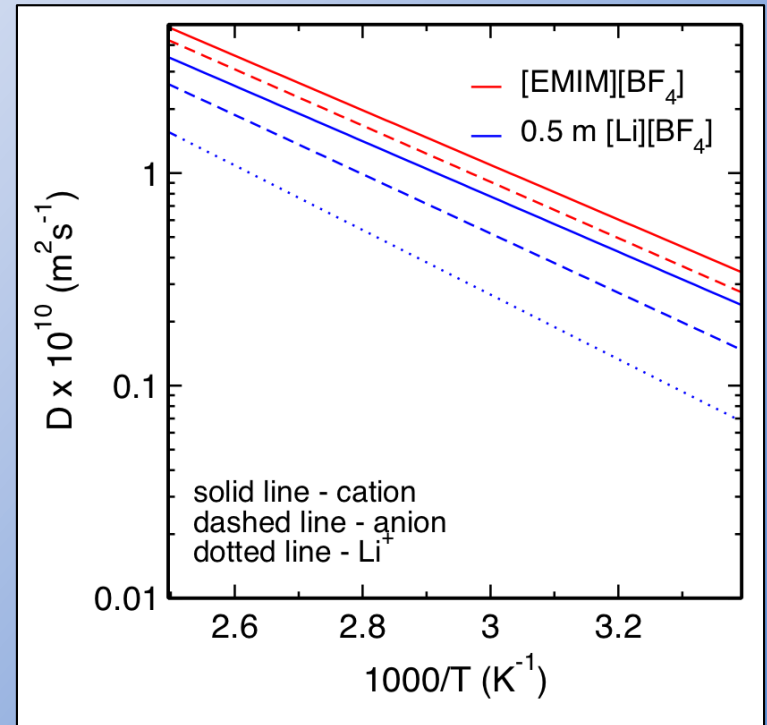
Diffusion coefficient

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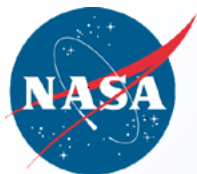
[pyr14][TFSI]



[EMIM][BF₄]

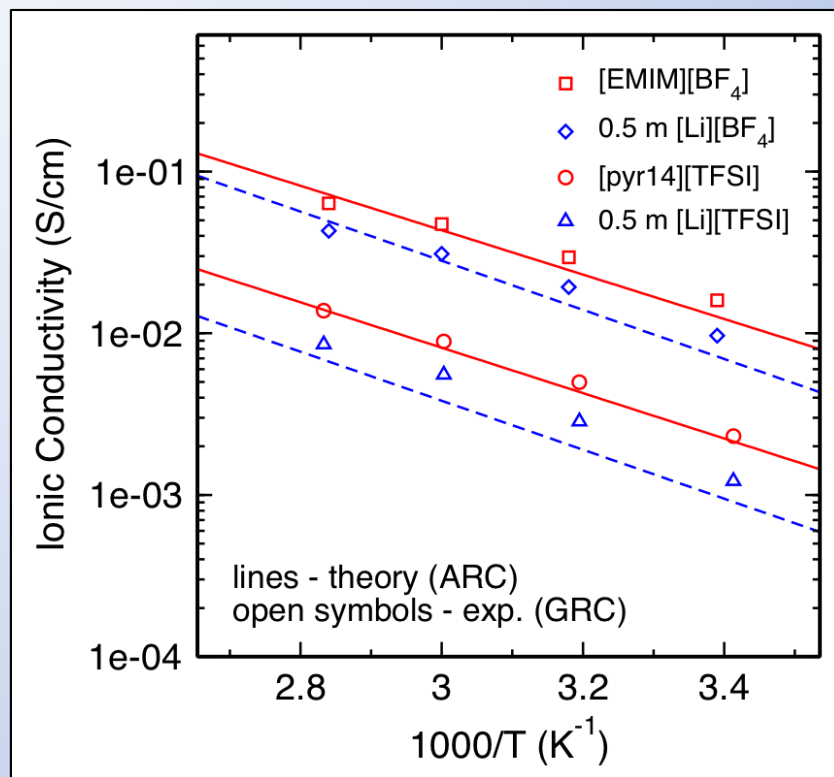


Diffusion data from GRC in progress



Ionic Conductivity

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Good agreement with GRC results

Conclusion: good agreement on broad range of electrolyte properties



Phase I Seedling

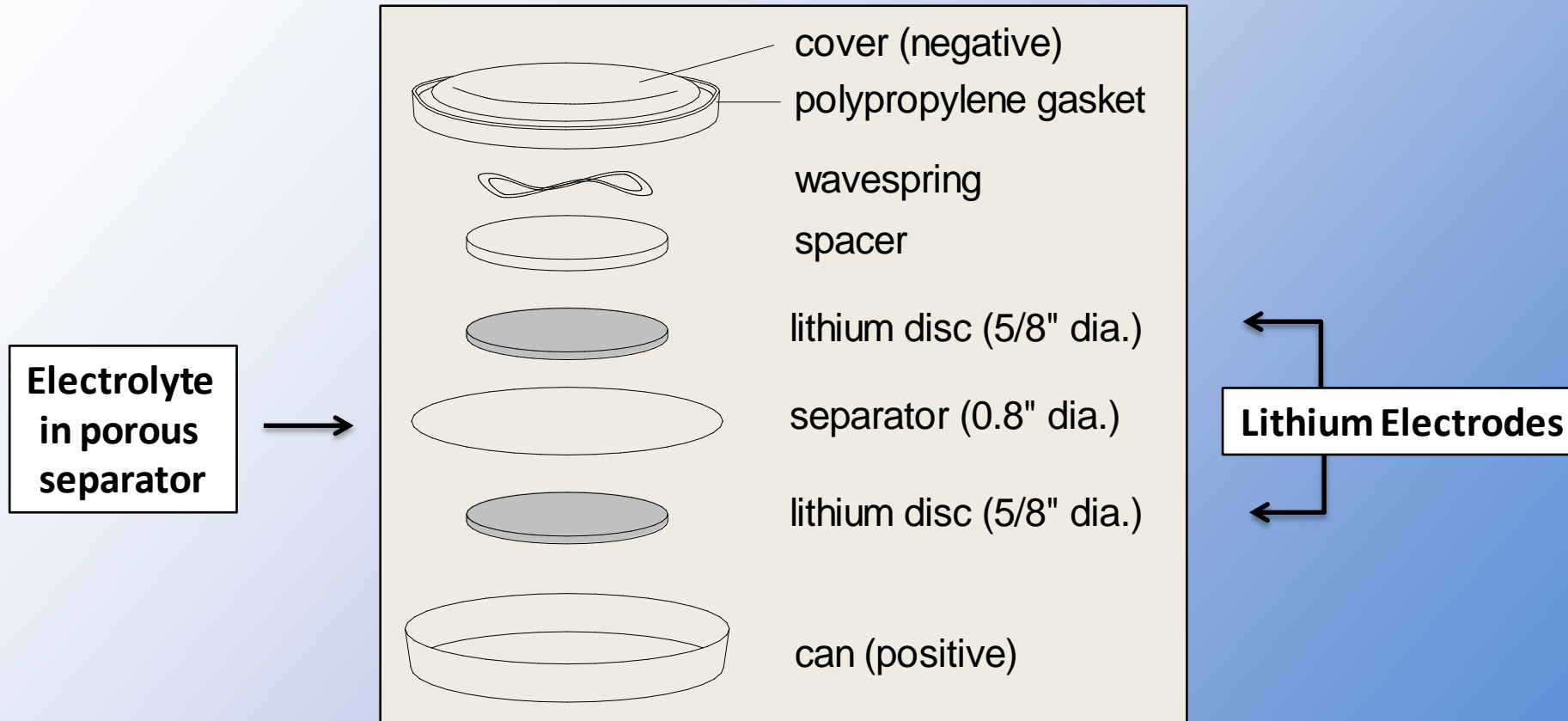
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- I. Isolated Ionic Liquids
- II. Experimental Cell Characterization**
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Lithium Coin Cell

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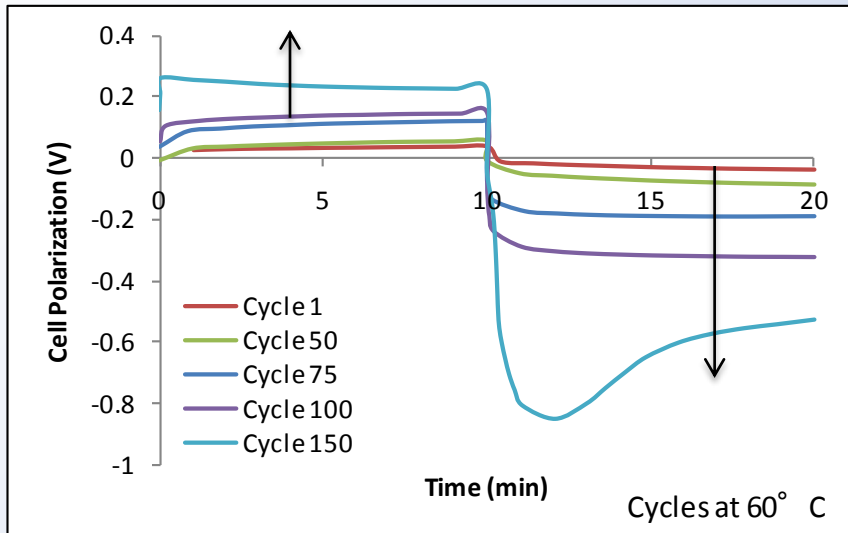
- Laboratory cells – easily constructed
- Focus characterization of the Li metal electrode



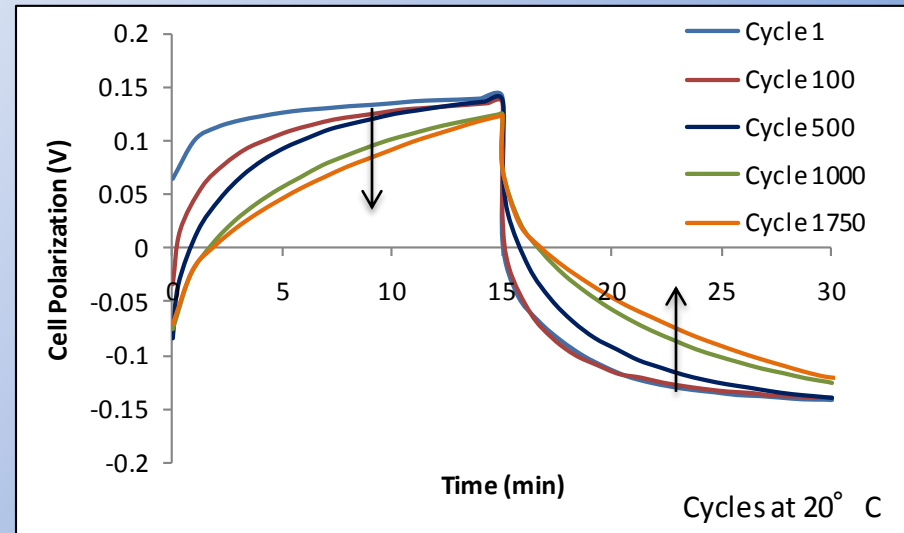
Cell Cycling

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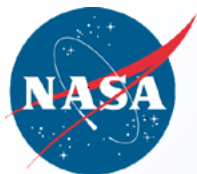
[EMIM][BF₄]



[pyr14][TFSI]

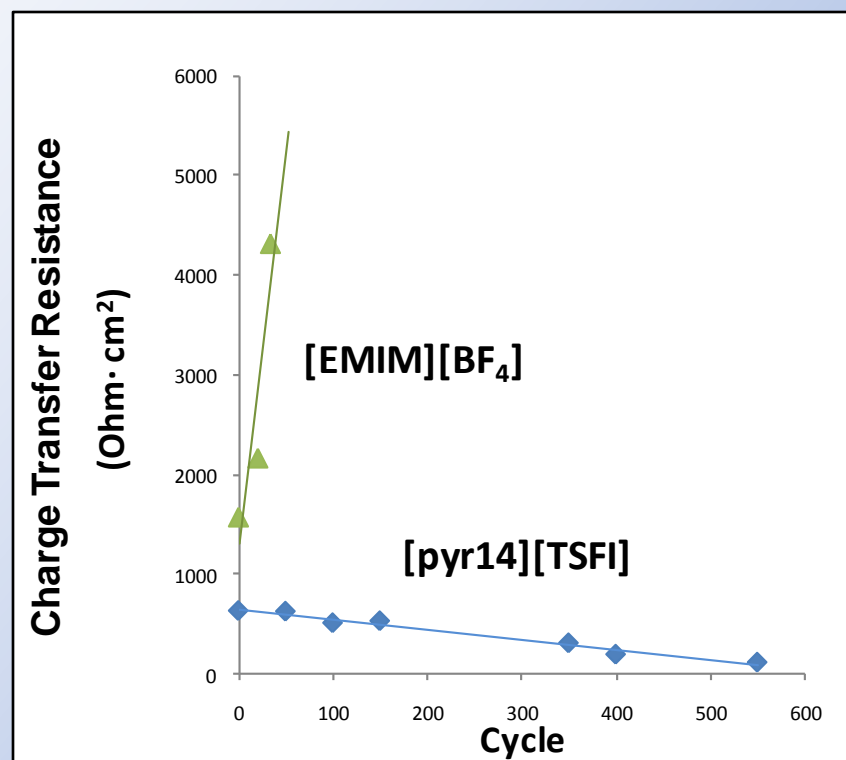


- [EMIM][BF₄] cell fails after **150** cycles
- [pyr14][TFSI] cell cycles successful up to **1750** cycles



Impedance Spectroscopy

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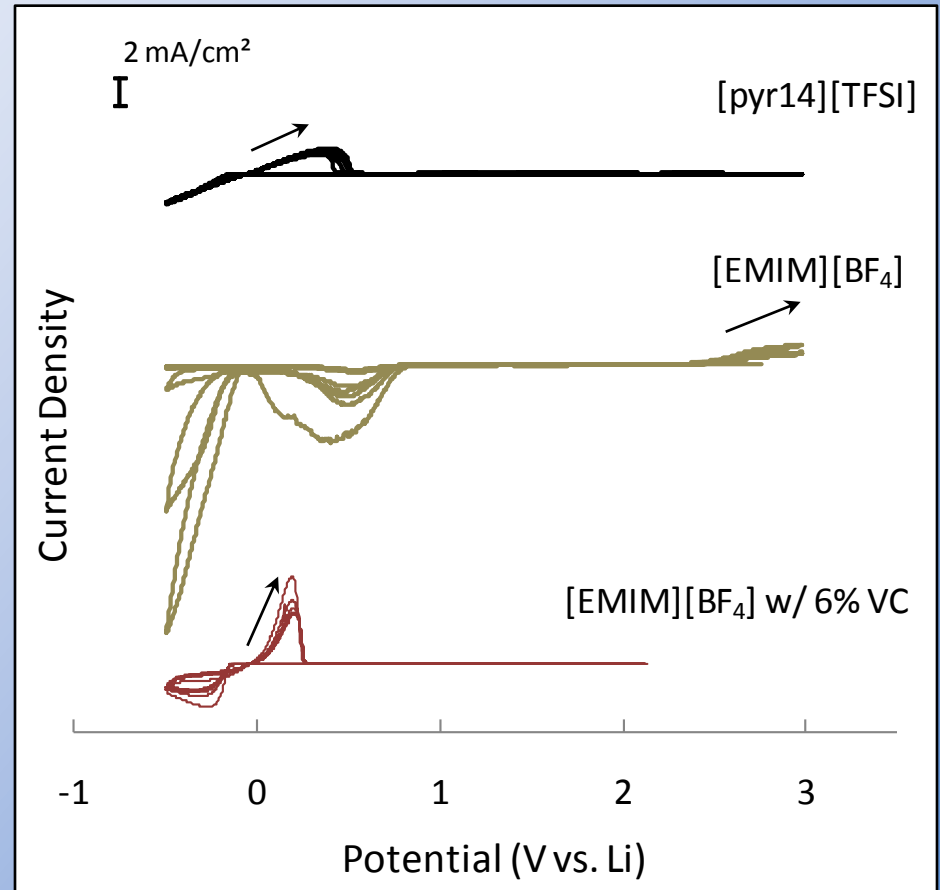
- [EMIM][BF₄] cell has ***increasing*** resistance
- [pyr14][TFSI] cell has ***decreasing*** resistance (increasing Li surface area)



Cyclic Voltammetry

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- [pyr14][TFSI] cell: **Li plating/stripping**
- [EMIM][BF₄] cell: **no Li stripping**
- [EMIM][BF₄] cell: **decomposition**
- Consistent with impedance data
- [EMIM][BF₄] cell with VC additive improves **Li plating/stripping**
- Decomposition explored in Phase II
- Additives to be explored in Phase II

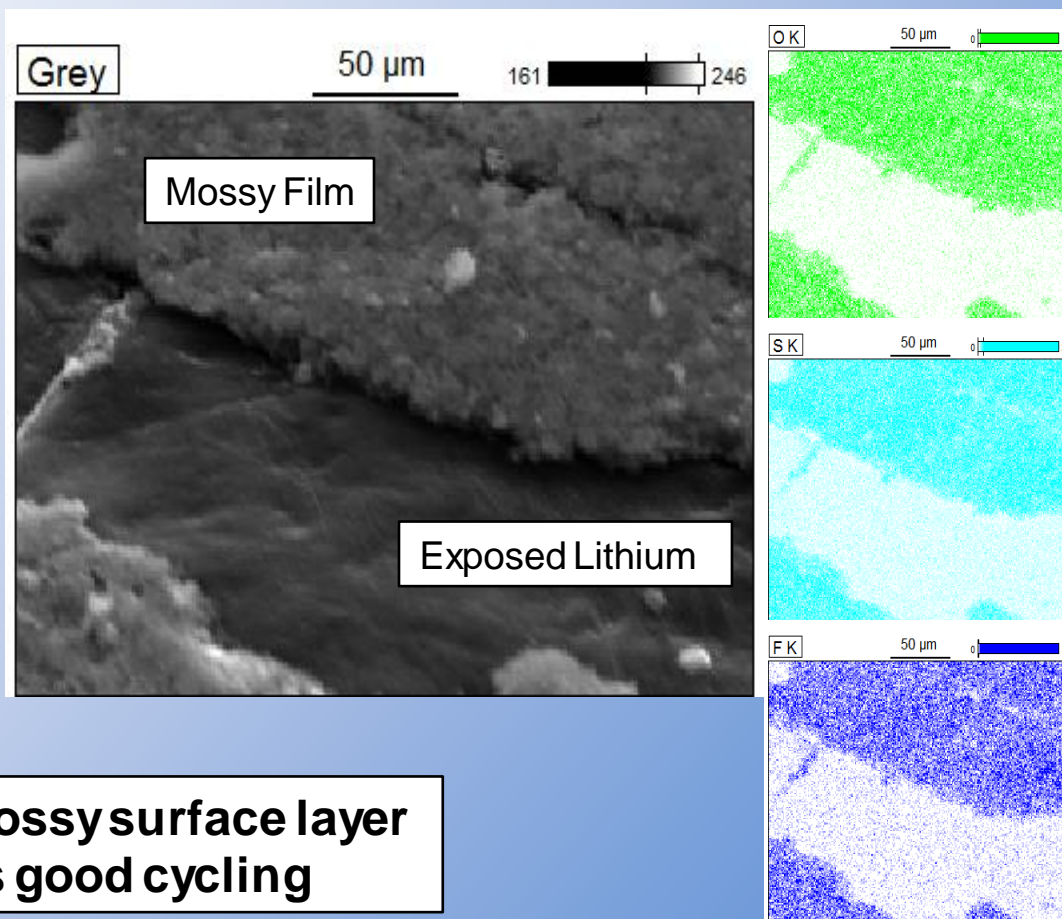




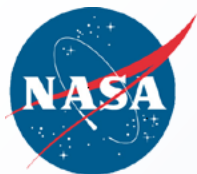
Surface Morphology: [pyr14][TFSI]

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- Li electrode after 1780 cycles
- ***“Mossy” Li deposits rich in electrolyte elements (O, S, F)***
- Smooth Li surface visible where mossy layer flaked off
- Mossy layer source of increased surface area
- ***Consistent with reduction in impedance***



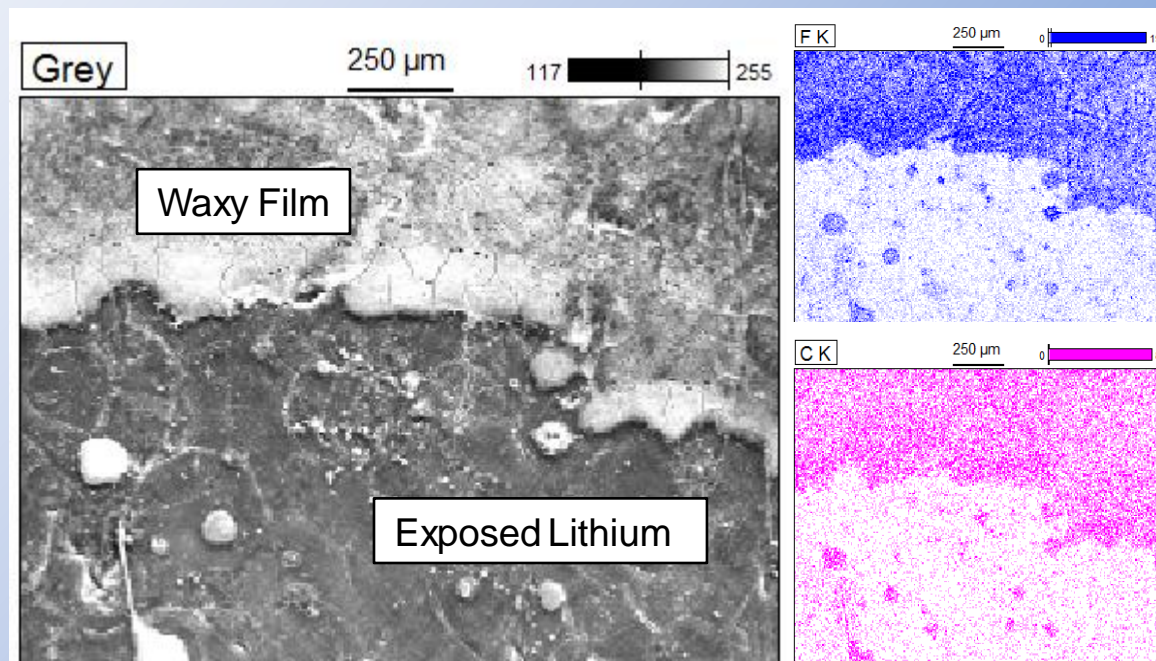
Conductive mossy surface layer facilitates good cycling



Surface Morphology: [EMIM][BF₄]

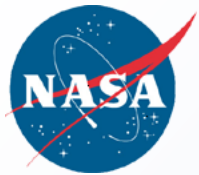
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- Li electrode after 130 cycles
- ***“Waxy” film covers ~75% of Li surface (rich in F and C)***
- Film consists of electrolyte decomposition products
- Li under film appears bright and un-utilized
- Reduction in active area
- ***Consistent with increase in impedance***



Insulating waxy surface layer results in poor cycling

Fundamental question: Why does one electrolyte give favorable surface layer and the other does not?



Phase I Seedling

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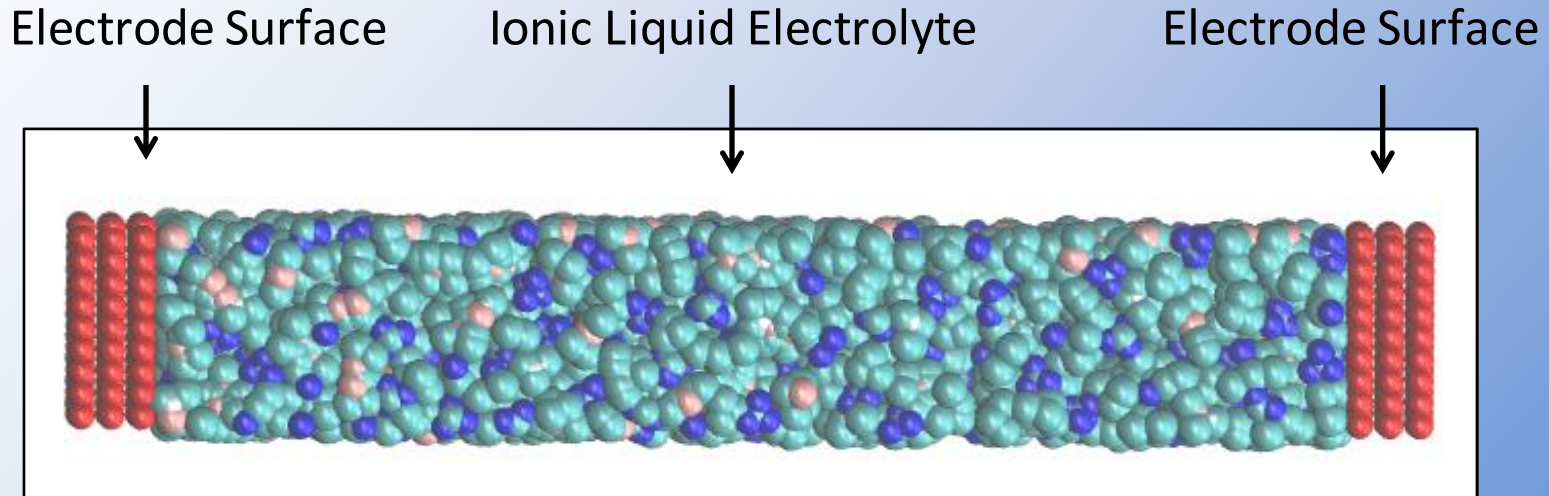
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Electrolyte-Electrode Interface

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Question: How does Ionic Liquid organize itself at electrode interface?

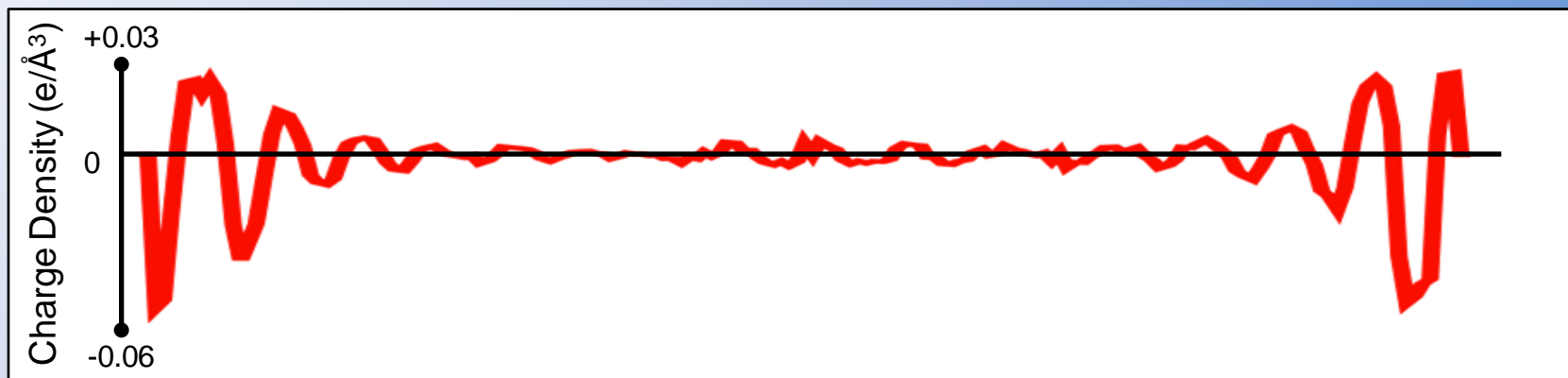
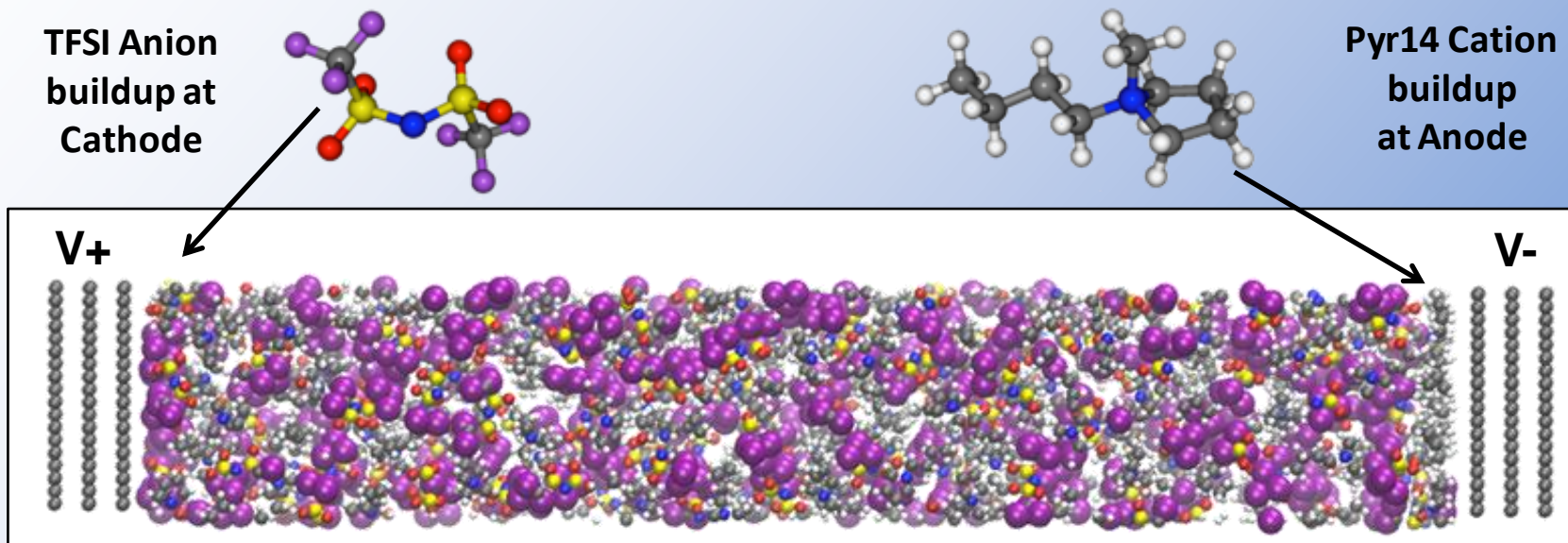


- Interface simulations with applied voltage (not milestone)
- ***Produced new (second) software module to be distributed***
- Full interface properties as function of voltage in Phase II



Electric Double Layer: [pyr14][TFSI]

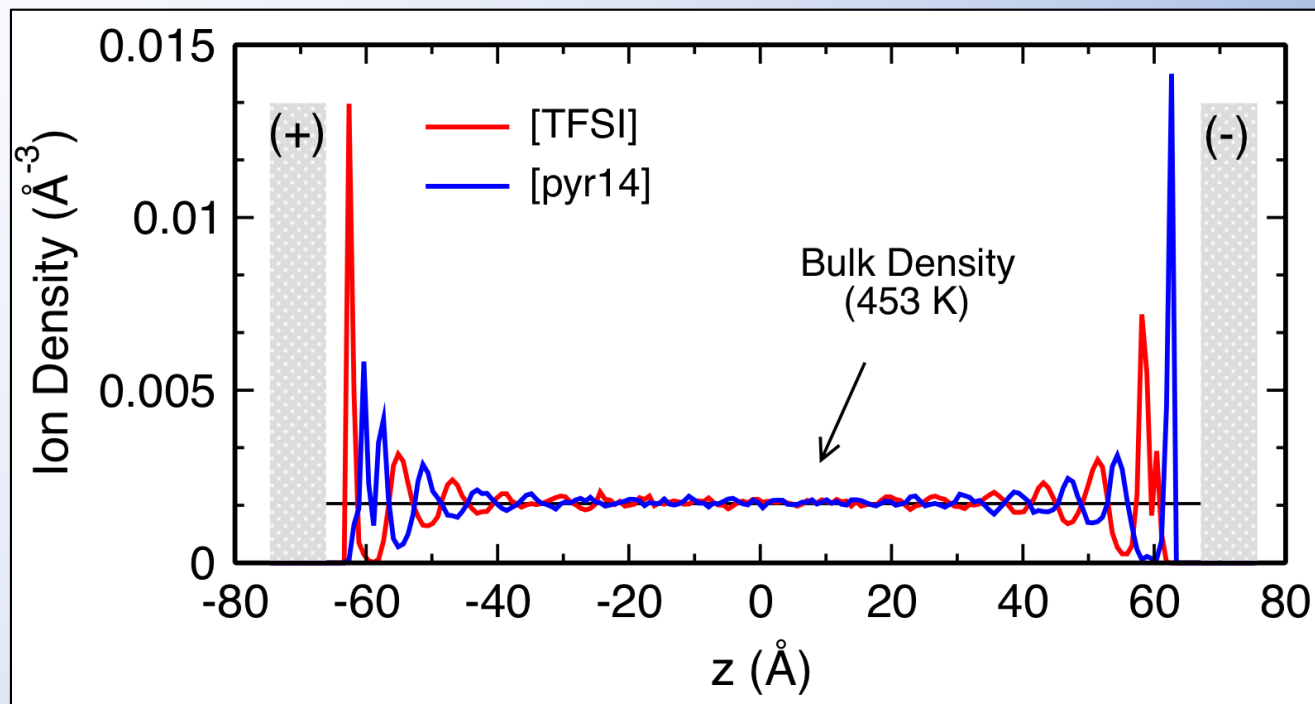
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Ion Density: [pyr14][TFSI]

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- Molecular layering near interface
- Classical theory predicts exponential decay

Conclusion: Molecular ordering near interface sets stage for interfacial reactions



Phase I Seedling

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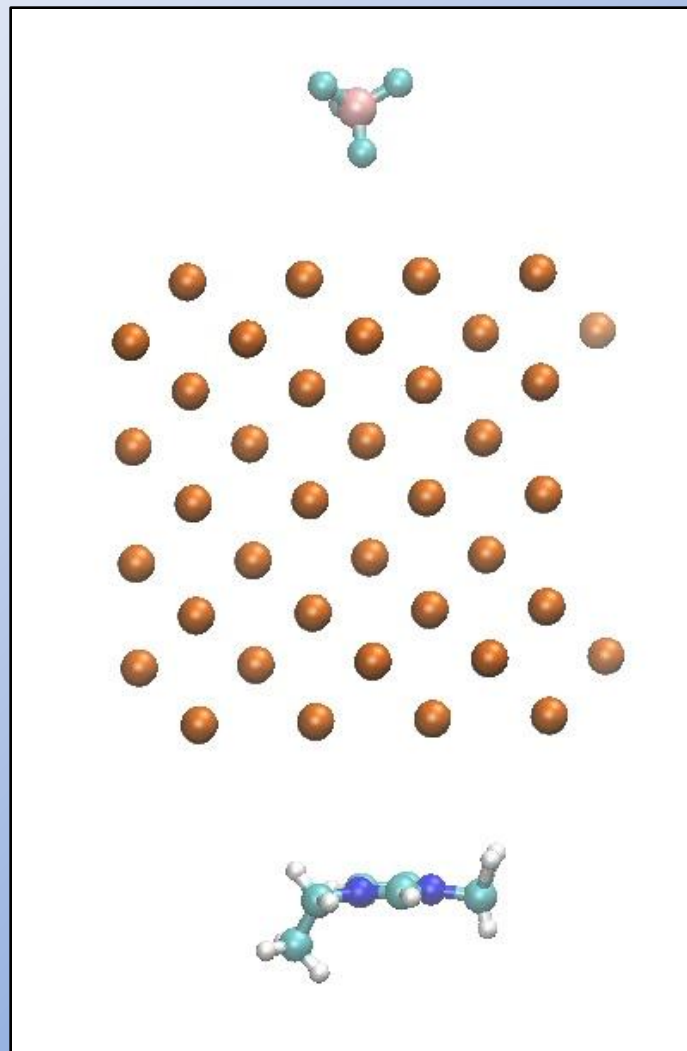
Surface Reactions: [EMIM][BF₄]

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Question: What are the chemical reactions and products between Li electrode and Ionic Liquid electrolyte?

***Ab Initio* Molecular Dynamics**

- High fidelity modeling
- Zero voltage
- Ions bound to surface
- ***No decomposition of ions***



**BF₄
anion**

**Lithium
slab**

**EMIM
cation**



Surface Reactions: [pyr14][TSFI]

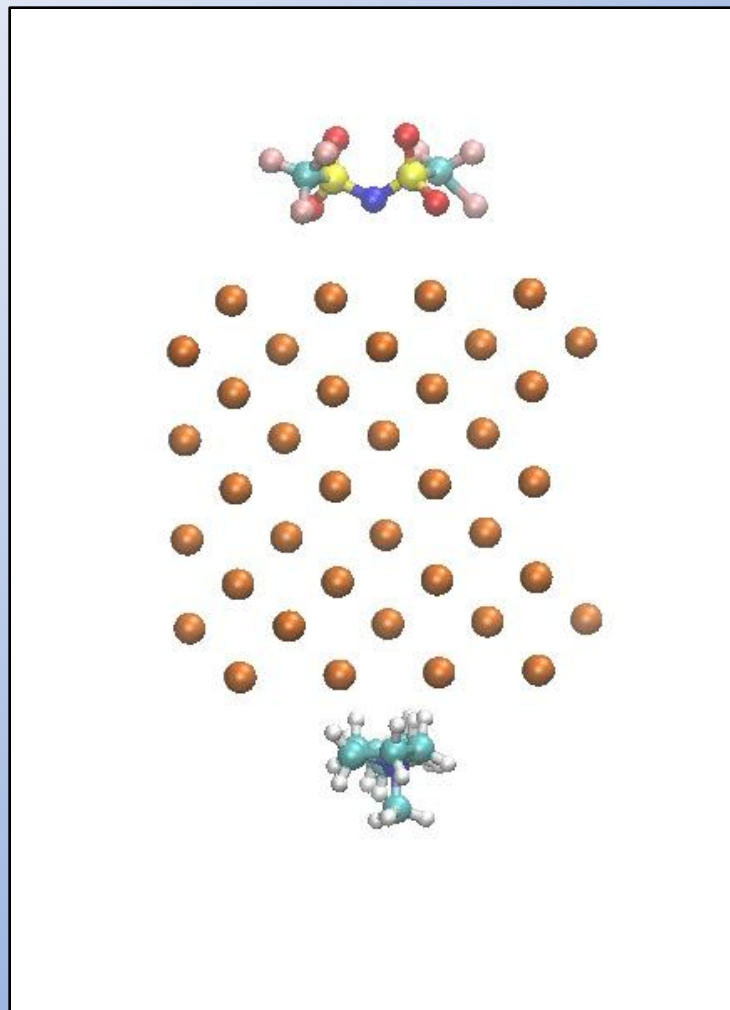
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***Ab Initio* Molecular Dynamics**

- High fidelity modeling
- Zero voltage
- Ions bound to surface
- Immediate decomposition of TSFI anion
- ***Screening tool for electrolytes(?)***

Conclusion: At zero voltage, very different anion decomposition behavior and products. Suggests that different surface layers will result (preliminary).

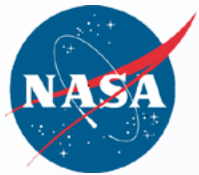
Phase II will consider surface reactions with applied voltage



**TSFI
anion**

**Lithium
slab**

**pyr14
cation**



Phase I Seedling

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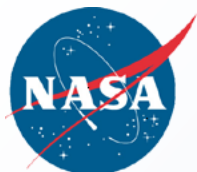
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Summary

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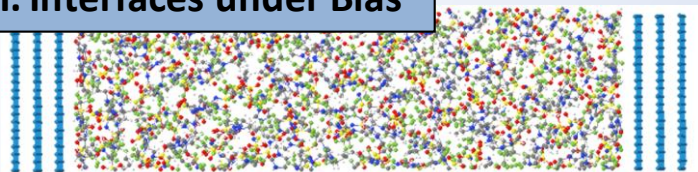
- **Phase I Major Accomplishments:**
 - Determined *transport properties* (computation/experiment) of two ILs
 - Built and characterized Li cells (cycling, impedance, voltammetry, SEM/EDAX)
 - Identified different surface layers for different electrolytes
 - Determined *interface double layer properties* (computation)
 - Identified *initial surface reactions* from simulations (computation)
- **Cross-Center, Multi-Disciplinary Team: ARC/GRC**
- **Benefit/Impact:** predictive tool tightly coupled to experiment for accelerated development of ultra high energy, safe batteries
- **Milestones:** We have met or exceeded all 12 milestones
- **Products:** two software modules to be distributed to community
- **Dissemination:** 3-4 journal articles plus conference presentations
- **Interest in Our Work:** DOE/ORNL, ARL, IBM Almaden Research
- **Spin-off Applications:** Ionic Liquids for Tribology, EPSCoR proposal



Future Directions

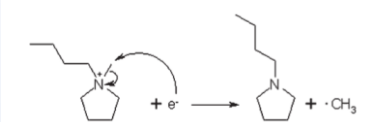
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I. Interfaces under Bias



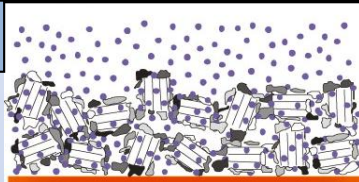
- Full interfacial properties vs voltage
- Measure interface capacitance

II. Surface Reactions under Bias



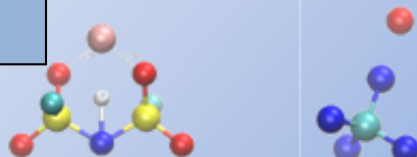
- Surface reactions vs voltage
- Compare to CV data

III. SEI growth simulations



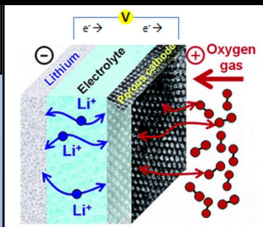
- Surface layer formation simulations
- Compare to SEM/EDAX data

IV. Electrolyte Optimization



- Additives and alternative ILs
- Modeling support of optimization

V. Full Cells: Cathode and Anode



- Build and characterize full cells
- **Optional:** Li-Air cell with IL electrolyte
- **Optional:** Oxidative stability modeling



Seedling Team

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- **GRC Electrochemistry Team**
 - Bill Bennett
 - James Wu
 - Tom Miller
 - Brianne Scheidegger
- **ARC Computational Modeling Team**
 - John Lawson
 - Justin Haskins
 - Charlie Bauschlicher
 - Josh Monk
 - Eric Bucholz
- **External Collaborators**
 - Oleg Borodin (ARL)
 - P. Ganesh (ORNL)
 - Prof. Farideh Jalilehvand (Univ of Calgary)
 - Prof. Mohsen Zaeem (Missouri Univ S&T)



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